INFLUENCE OF ELECTRONIC STRUCTURE ON THE MAGNETIC PROPERTIES OF IV-VI DILUTED MAGNETIC SEMICONDUCTORS

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13. ABSTRACT (Maximum 200 words)

We investigated the magnetic and thermal properties of chalcogenide-based diluted magnetic semiconductor (DMS) systems. These systems have been considered as possible novel materials with increased magnetic sensitivity and thermoelectric efficiency. Measurements of the magnetic properties of $Sn_{1-x}Gd_xTe$ show that there is an antiferromagnetic pair-exchange interaction with a maximum in the magnitude at a hole concentration of about 3×10^{20} cm^{-3}. The interpretation of this result is based on the relative positions of the Gd 5*d* level, the Fermi level, and the L and Σ levels in the valence band. We have also measured the low-temperature specific heat in these DMS systems. Theoretical calculations have shown that one must take into account the systems of magnetic ions and the carriers and the interactions between them in order to obtain an approximate fit to the data. We have performed measurements of the thermoelectric power, thermoelectric figure of merit, and electrical conductivity in $Pb_{1-x}Mn_xTe$. The thermoelectric power increased as the Mn-content increased, but a decrease in the carrier mobility limited the thermoelectric figure of merit. In new quaternary and pentenary DMS we have observed a paramagnet – ferromagnet transition and a temperature dependent anomalous Hall effect.

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Diluted magnetic semiconductor, chalcogenide, exchange interaction, antiferromagnetic, magnetization, susceptibility, specific heat, thermoelectric power, thin film, heterostructure.

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Keywords: diluted magnetic semiconductor, chalcogenide, exchange interaction, antiferromagnetic, magnetization, susceptibility, specific heat, thermoelectric power, thin film, heterostructure.

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I. INTRODUCTION

Previous investigations of IV-VI DMS systems of the form $A_{1-x}M_xB$, where A is an element from column IV in the Periodic Table, B is from column VI, and M is a magnetic ion, such as Mn or a rare earth, substituting for the cation, have shown that the magnetic ions strongly influence the electronic structure. For example the carrier g-factor changes with the addition of the magnetic component and becomes magnetic field dependent. In the present project we are examining the converse, i. e. the influence of the electronic structure on the magnetic properties. The ability to control magnetic properties by varying electronic properties may have applications in detection and measurement of magnetic fields and in long-wavelength optical devices such as diode detectors and those based on Faraday rotation. Therefore, we have undertaken studies to characterize the physical properties of these systems. These DMS materials, as grown by the Bridgman technique, have large concentrations of holes, which can be reduced by annealing in an appropriate vapor. For example SnTe-based systems may have as-grown hole concentrations of the order of 10^{21} cm^{-3}, which can be reduced by annealing in Sn vapor. These high hole concentrations have been attributed to Sn vacancies. This characteristic allows one to study the variation of a material's physical properties with carrier concentration *in just one sample.* We have taken advantage of this feature in our present research on magnetic properties in order to study the dependence of the pair exchange interaction on carrier concentration and x-value.

Materials like PbTe are used in space for thermoelectric generators to produce electrical power from heat sources such as radioactive isotopes or nuclear reactors. Such thermoelectric generators have very low efficiency, but they are the best we have for this purpose at the present time. It has been suggested, however, that the addition of a magnetic component might enhance the thermoelectric power. In order to examine the potential of $A_{1-x}M_xB$ systems for such purposes, we are investigating their thermal and thermoelectric properties. We have begun with measurements of the heat capacity in $Pb_{1-x}Mn_xTe$ since approximately the same measuring system will be appropriate for thermoelectric measurements and Mn gives a large exchange interaction compared to rare earths. We have found a significant magnetic contribution to the heat capacity at low temperatures, but the theoretical interpretation, to be discussed below, is at a very preliminary stage. We also report on our preliminary measurements of the thermoelectric figure of merit, ZT. Here T is the temperature and $Z = \alpha^2\sigma/\kappa$ where α is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity.

It has been proposed that thermoelectric properties might be enhanced by the use of heterostructures.[2] We will also describe below our molecular beam epitaxy (MBE) system for preparing thin films and the types of structures that have been grown up to the present time.

We have prepared a range of new quaternary and quinary IV-VI DMS with two magnetic cations and one or two nonmagnetic cations. We have performed preliminary studies of the magnetic and transport properties of these materials. A paramagnet - ferromagnet phase transition due to the RKKY interaction has been observed below T = 10 K in materials with carrier concentration above 3×10^{20} cm^{-3}.

II. MAGNETIC PROPERTIES

During the period of our report we focused on $Sn_{1-x}Gdn_xTe$ because it has a high density of carriers, holes, as grown and this density can be changed by at least a factor of 10 by appropriate annealing. We have measured the magnetization of p-type $Sn_{1-x}Gd_xTe$, with x up to 0.1 and hole concentrations varying from 0.9 to 8.3 × 10^{20} cm^{-3}, in high magnetic fields. The samples were grown at the Institute of Physics of the Polish Academy of Sciences by the Bridgmann technique and the Gd concentration was determined by electron microprobe (energy dispersive x-ray analysis) and from the lattice constant measured by powder x-ray diffraction. We studied the high-field magnetization at temperatures down to 1.2 K and fields up to 33 T and the low temperature magnetization at temperatures down to 30 mK and fields to 18 T at the High Magnetic Field Laboratory in Tallahassee. No magnetization steps were observed even at temperatures of 30 mK. Although we did not see steps in the magnetization, the low-field magnetization at mK temperatures increased nearly linearly with magnetic field, unlike the Brillouin-function type of behavior that we see at higher temperatures. We were able to determine the pair exchange interaction by fitting to our data. This exchange interaction reached a maximum at a hole concentration of about 3.1 × 10^{20} cm^{-3} and decreased with concentrations larger and smaller than this value as shown in Fig. 1. This result has been attributed to the location of the Fermi level and the Gd 5*d* level close to each other and to the top of the valence band Σ. We propose that the pair exchange interaction between the *f* levels on neighboring Gd ions takes place via the *d* levels as an f_1-d_1-sp-d_2-f_2 interaction of the RKKY type, where 1 and 2 refer to the neighboring magnetic ions.[1] We also suggest that the absence of steps implies a smearing out of the exchange interaction as a result of the relatively long range of this interaction. These results have been reported recently in Phys. Rev. B. [1]

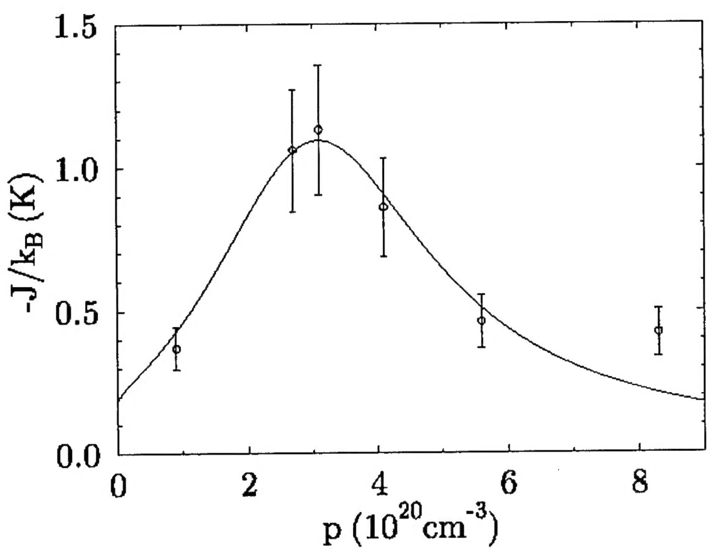

Fig. 1. Exchange parameter vs hole concentration in $Sn_{1-x}Gd_xTe$.
The solid line is the fit to the Lorentzian-type expression,
($-J/k_B = 1.01/((p^{2/3} - (3.1)^{2/3}) + (0.96)^{2/3}.$)

In $Sn_{1-x}Gdn_xTe$ the exchange interaction is antiferromagnetic, but it does depend on the carrier concentration. However, other IV-VI DMS containing Mn exhibit both antiferromagnetic and ferromagnetic exchange interactions depending on the carrier concentration as we summarize schematically in Fig. 2. At concentrations somewhat greater than 3×10^{20} cm^{-3} the interaction is ferromagnetic and is antiferromagnetic below this value as indicated by the vertical line in the figure. This carrier concentration induced antiferromagnetic – ferromagnetic transition has been explained by attributing the ferromagnetic interactions in IV-VI DMS to the Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism of indirect exchange via conducting holes. The ferromagnetic interaction is observed above the hole concentration about 3×10^{20} cm^{-3} at which the Fermi level enters the band of heavy holes, Σ. This model has been described in our earlier papers.[3,4]

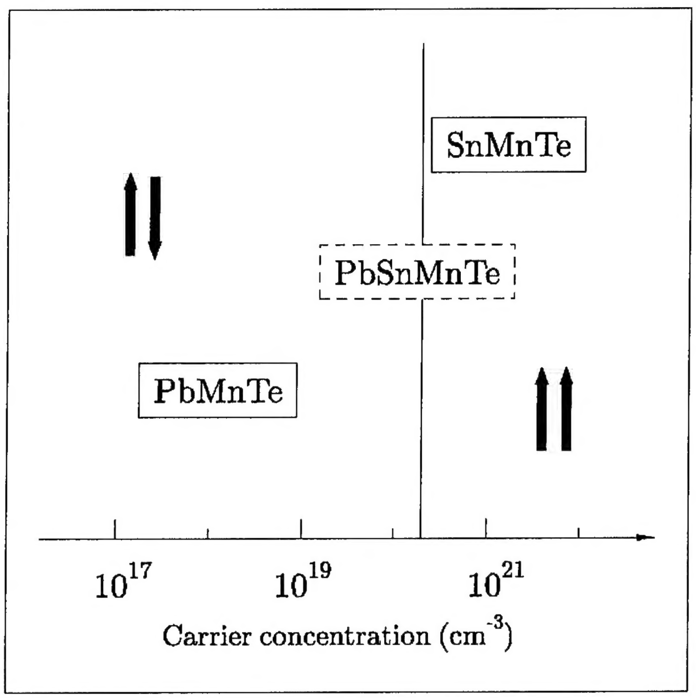

Fig. 2. Influence of density of carriers on the magnetic behavior of Mn-based IV-VI DMS.

III. MAGNETIC SPECIFIC HEAT

In order to develop a more complete model and to obtain parameters for the exchange interaction, we have made complementary measurements of the magnetic specific heat. Up to now, no experimental data on the magnetic contribution to the specific heat of $Pb_{1-x}Mn_xTe$ have been available. Therefore, in this work we examined the temperature and magnetic-field dependence of the magnetic contribution to the specific heat of $Pb_{1-x}Mn_xTe$.

We have measured the specific heat of $Pb_{1-x}Mn_xTe$ with x values of 0.024 and 0.056. The samples were grown by the Bridgman technique at the Institute of Physics of the Polish Academy of Sciences. The Mn content in the samples was determined by X-ray energy fluorescent dispersive analysis with an accuracy of about 7 % of the x-value. We did not see any peaks corresponding to phases other than the rock salt crystal of $Pb_{1-x}Mn_xTe$. Carrier concentrations and mobilities were determined by the Hall effect and conductivity measurements. All samples were p-type. At 77 K the hole concentration both for $x = 0.056$ and $x = 0.024$ was about 3×10^{18} cm^{-3}, and the hole mobility was about 2.5×10^3 cm^2/V s. The measurements of the heat capacity were also performed at the Institute of Physics of the Polish Academy of Sciences. The heat capacity was measured in a cryostat using a ^{3}He or ^{4}He system, over the temperature range 0.5 - 15 K, in magnetic fields 0, 0.5, 2, and 4 T. We used the standard adiabatic heat-pulse method. In order to obtain the magnetic contribution to the specific heat, C_m, it was necessary to subtract the specific heat of the PbTe lattice from the measured specific heat of $Pb_{1-x}Mn_xTe$. We measured the heat capacity of our own PbTe sample, which was also grown by the Bridgman method. At temperatures below 4 K the heat capacity of PbTe was very small and we found it necessary to measure by the relaxation method; above 4 K it was possible to use the same adiabatic method as we used for $Pb_{1-x}Mn_xTe$.

The magnetic contribution to the specific heat in zero magnetic field had a maximum at about 1 K for x=0.056; this peak shifted to higher temperatures in magnetic fields, but remained approximately the same height. The same field dependence was observed for x=0.024. To explain the experimental results several theoretical models have been tested and calculation performed. The best agreement with the data was obtained by taking into account the whole magnetic ion system, the whole free carrier system, and the interaction between them. The experimental and theoretical results for our $Pb_{1-x}Mn_xTe$ sample with x=0.056 are shown in Fig. 3. Preliminary results of this research have been submitted for publication [2]. The theoretical work is still in progress.

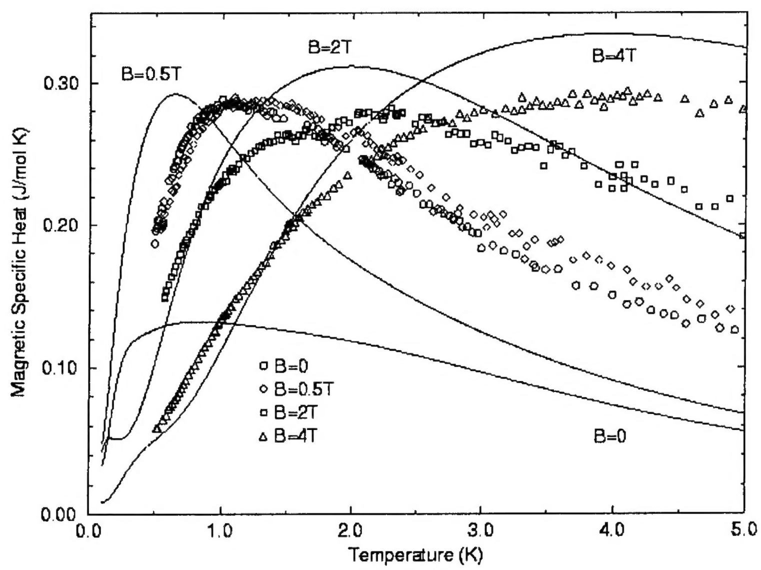

Fig. 3. Magnetic specific heat of $Pb_{1-x}Mn_xTe$ with x=0.056. Markers – experimental data, lines – theoretical calculation.

IV. THERMOELECTRIC PROPERTIES

PbTe is a well known good thermoelectric material which found applications, e.g. in U.S. space program. However, even for the technologically optimized material, the highest value of thermoelectric figure of merit parameter $ZT \approx 0.45$ at room temperature. Also, for other thermoelectric materials, like Si-Ge, or Bi_2Te_3 – based alloys $ZT < 1$, which seriously limits the field of applications of semiconductor thermoelectric devices.

In this project we examined the thermoelectric parameters of IV-VI diluted magnetic semiconductor $Pb_{1-x}Mn_xTe$ with $x \leq 0.08$. Our motivation was based on our first results of the thermoelectric power measurements in p-$Pb_{1-x}Mn_xTe$ (the Seebeck coefficient, α, was increasing about 2.5 times, from 250 μV/K for x = 0 to 600 μV/K for x = 0.08.) This result is shown in Fig. 4. We hoped to obtain new thermoelectric materials with figure of merit above 1 at room temperature. We have checked with Hall effect measurements that the concentration of conducting holes in our $Pb_{1-x}Mn_xTe$ crystals was $p = 2 \times 10^{18}$ cm^{-3} and was practically Mn-content independent. Since we were interested in room temperature carrier mobility, we expected that the incorporation of Mn will lower the mobility, but it will be not a dramatic effect. However, the further direct measurements of ZT, based on the comparison of resistivity in the dc (Peltier effect present) and ac (Peltier effect absent) regime, showed that ZT decreased from 0.21 for x = 0 to 0.05 for x = 0.08 (see Fig. 5).

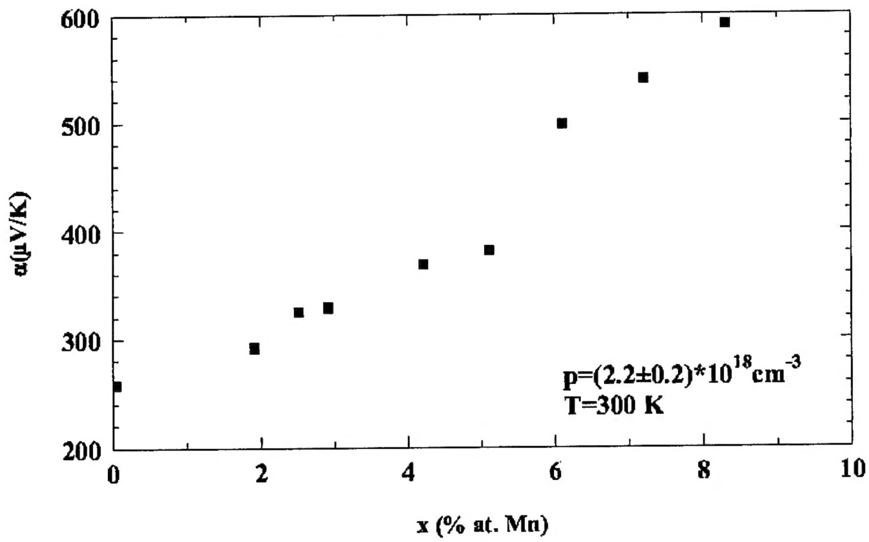

Fig. 4. Thermoelectric power in p-$Pb_{1-x}Mn_xTe$

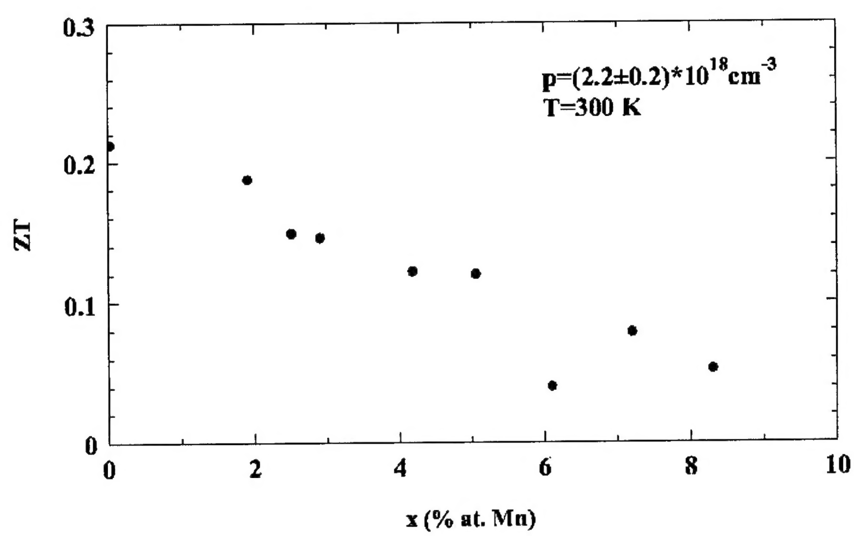

Fig. 5. Thermoelectric figure of merit in p-$Pb_{1-x}Mn_xTe$.

In order to understand this decrease of ZT with increasing Mn-content we measured the Hall effect and electrical conductivity in these materials, and determined the carrier mobility. The results have shown that the room temperature mobility strongly decreased with increasing Mn-content from 380 cm^2/Vs for x = 0 to 13 cm^2/Vs for x = 0.08. As a consequence the electrical conductivity also decreased, as is shown in Fig. 6. We assume that the decrease in the electrical conduction may be connected with scattering on the crystalline grain boundaries.

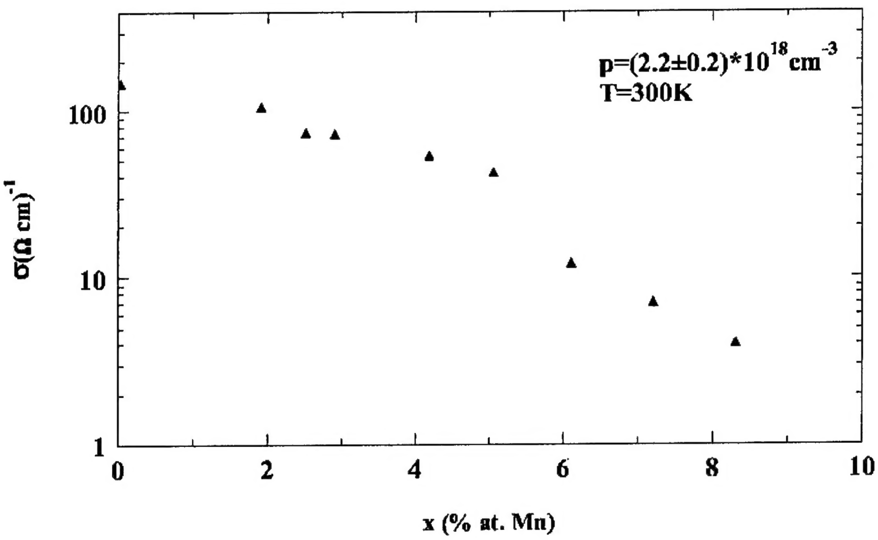

Fig. 6. Electrical conductivity in p-$Pb_{1-x}Mn_xTe$.

Next, we attempted to increase ZT by means of annealing the samples with different Mn-content in Te vapor. However, though for the as-grown crystal a higher value of ZT (0.25) was obtained for pure p-PbTe, for $Pb_{1-x}Mn_xTe$ with x = 0.08 the value of ZT remained similar to the as-grown sample and equaled about 0.05 (mobility was higher but α lower).The further development of new thermoelectric materials based on PbMnTe depends crucially on the growing of crystals with room temperature mobilities limited by phonon and alloy scattering only.

We have also studied thermoelectric power in $Pb_{1-x-y}Sn_yMn_xTe$ DMS with x = 0.12 and y = 0.72 in the temperature range T = 10 - 100 K, covering both the ferromagnetic and paramagnetic range of temperatures in this material. In addition to the standard diffusion contribution to the thermoelectric power, $\alpha_D(T)$, we found in PbSnMnTe an additional "magnetic" contribution, α_{FM}. Employing the effect of carrier-concentration-controlled ferromagnetism in PbSnMnTe, we demonstrated that the temperature dependence of $\alpha_{FM}(T)$ shows a clear maximum at the ferromagnetic Curie temperature. The effect was of an order of 5 μV/K. This experimental finding was discussed in terms of Kasuya model for the thermoelectric properties of diluted magnetic metallic systems with *sd*-exchange interaction.[5] These results have been submitted for publication [3].

V. THIN FILMS

Hicks, Harman, Sun, and Dresselhaus suggested that semiconductor quantum wells would have an improved figure of merit.[6,7] They showed theoretically, and confirmed experimentally using the PbTe quantum wells confined by $Pb_{0.927}Eu_{0.073}Te$ barrier layers, that ZT for a single quantum wells increases as the well width decreases. Recently, we started preparing thin films of IV-VI DMS in our home-built molecular beam epitaxy (MBE) system. We have grown layers of $Pb_{1-x}Mn_xTe$ on BaF_2 substrates. The Mn-content was up to 0.02, and the layer thickness up to 4μm. We found that in some layers the α was somewhat greater than in bulk materials, but the conductivity did not improve significantly. This work is at a very preliminary stage.

We also continued the investigation of the magnetic properties of SnTe-based DMS in thin films. Thin layers of $Sn_{1-x}Mn_xTe$ with Mn content $x \leq 0.04$ and layer thickness 0.2 - 2 μm were grown by MBE on BaF_2 (111) substrates with SnTe buffer layer. Apart from SnTe and Mn fluxes, we employed an additional Te flux to provide the efficient way of controlling the deviation from stoichiometry in the layers. A typical heterostructure is shown in Fig. 7.

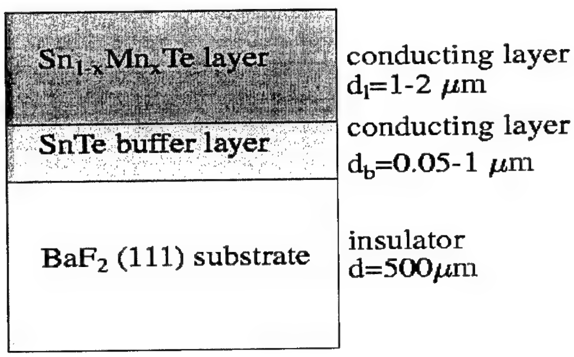

Fig. 7. Typical design of a $Sn_{1-x}Mn_xTe$/SnTe heterostructure.

For the electrical characterization of the layers, we performed standard dc measurements of Hall effect and electric conductivity in the temperature range T = 4.2 - 300 K applying magnetic fields $B \leq 1.2$ T. The quantitative analysis of the experimental data was somewhat obscured due to the presence of the highly conducting SnTe buffer layer. We found that by manipulating the MBE growth conditions it was possible to obtain $Sn_{1-x}Mn_xTe$ crystalline layers with the conducting hole concentration in the range from $p = 5 \times 10^{19}$ cm^{-3} (no extra Te flux) to $p = 2 \times 10^{21}$ cm^{-3} (additional Te flux present).

The magnetic susceptibility, χ, of $Sn_{1-x}Mn_xTe$ layers was studied at the Institute of Physics with a LakeShore mutual inductance susceptometer operating in the temperature range T = 1.4 - 300 K, applying a low ac magnetic field typically of 1 Oe at a frequency of 625 Hz. In the layers grown under extra Te flux conditions we observed a ferromagnetic exchange interaction with the Curie temperature $T_C \leq$ K (depending on both x and p). Layers with the

same Mn content but grown with no extra Te flux were paramagnetic. This behavior was similar to that observed before in bulk materials and shown schematically in Fig. 2. It seems that the same mechanism of carrier induced paramagnetic – ferromagnetic transition occurs both in bulk and thin films IV-VI DMS. The results have been submitted for publication [4].

VI. NEW QUATERNARY AND QUINARY IV-VI DMS.

The batch of ingots of new IV-VI DMS containing Eu, Yb, and Er in addition to Mn magnetic ions was prepared by modified Bridgman method. The $Pb_{1-x-}yMn_xEu_yTe$ ($0.005 \leq x \leq 0.05$, $0 \leq y \leq 0.006$), $Pb_{1-x-y-z}Mn_xEu_ySn_zTe$ ($0.021 \leq x \leq 0.031$, $0.001 \leq y \leq 0.017$, $0.682 \leq z \leq 0.850$) and $Sn_{1-x}Mn_xEu_yTe$ ($x \leq 0.15$, $y \leq 0.02$) crystals were investigated by x-ray Debye powder method. They were found free of second phase inclusions with the cubic lattice constant equal to 6.4465Å, 6.3427Å for $Pb_{0,991}Mn_{0,005}Eu_{0,004}Te$, $Pb_{0,267}Mn_{0,025}Eu_{0,014}Sn_{0,694}Te$, respectively. The chemical composition of the samples was determined by x-ray dispersive fluorescence analysis technique. In Fig. 8 we show as an example a concentration profile of Eu, Mn and Sn content for one ingot.

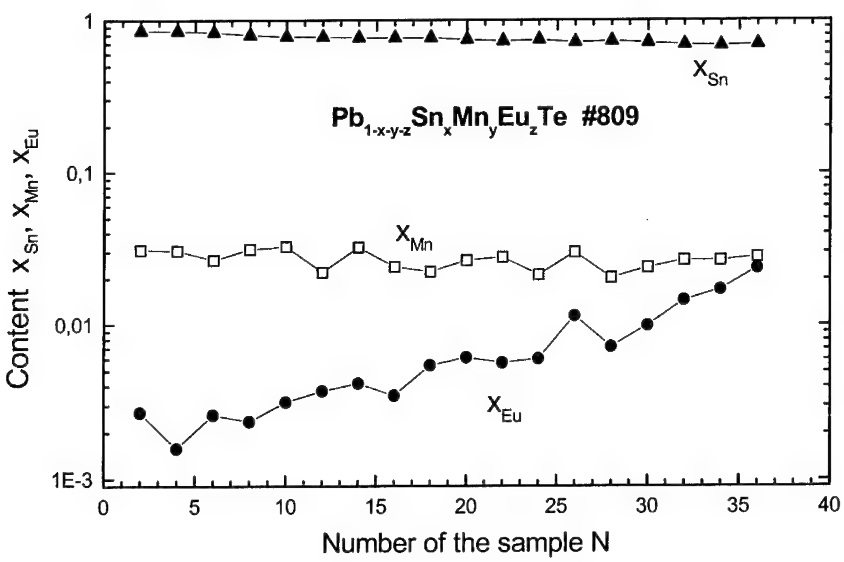

Fig. 8. Concentration profile in a $Pb_{1-x-y-z}Mn_xEu_ySn_zTe$ ingot

The crystals of $Pb_{1-x-y}Ge_xEu_yTe$, (technological content of Ge = 0.01,0.1, and Eu = 0.01), $Sn_{1-x-y}Mn_xEr_yTe$ (technological content of Mn = 0.1 and Er = 0.005 and $Pb_{1-x-y}Sn_xYb_yTe$, (technological content of Sn = 0.03, and Yb = 0.01), are currently investigated in order to determine real composition and crystallographic structure. Crystals are investigated by means of x-ray dispersive fluorescence analysis technique and powder Debay technique. The investigation of transport and magnetic properties of these materials is planned in the near future.

Hall effect and conductivity measurements of $Pb_{1-x-y}Mn_xEu_yTe$, $Pb_{1-x-y-z}Mn_xEu_ySn_zTe$ and $Sn_{1-x-y}Mn_xEu_yTe$ crystals were performed at room, liquid nitrogen, and liquid helium temperature. All investigated samples occurred to be *p*-type with high (2.3×10^{18} cm^{-3} < p < 4.8×10^{20} cm^{-3}, 3.18×10^{20} cm^{-3} < p < 1.0×10^{21} cm^{-3} for $Pb_{1-x-y}Mn_xEu_yTe$ and $Pb_{1-x-y-z}Mn_xEu_ySn_zTe$ (or $Sn_{1-x-y}Mn_xEu_yTe$), respectively, at $T = 300$ K) and practically temperature independent concentration of carriers.

Magnetic susceptibility and magnetization of $Pb_{1-x-y}Mn_xEu_yTe$, $Pb_{1-x-y-z}Mn_xEu_ySn_zTe$ and $Sn_{1-x-y}Mn_xEu_yTe$ were investigated in the temperature range 1.3-150 K using a mutual inductance method. The measurements were carried out in ac magnetic field of frequency in the range 7-10000 Hz and amplitude not exceeding 5 Oe. In the case of $Pb_{1-x-y}Mn_xEu_yTe$ the obtained results indicated that the dominant mechanism in $Pb_{1-x-y}Mn_xEu_yTe$ crystals was a weak antiferromagnetic superexchange interaction. The second group of samples, $Pb_{1-x-y-z}Mn_xEu_ySn_zTe$ and $Sn_{1-x-y}Mn_xEu_yTe$ was characterized by substantially larger carrier concentration. In these crystals at low temperatures the phase transition to ferromagnetic /or spin glass-like phase takes place. This behavior is, again, similar to that shown in Fig. 2. for DMS with Mn only. The obtained results indicate that with an increase of the Eu-content the value of the Curie temperature decreases. In Fig. 9 is shown the dependence of magnetic susceptibility on temperature in a series of $Pb_{1-x-y-z}Mn_xEu_ySn_zTe$ samples.

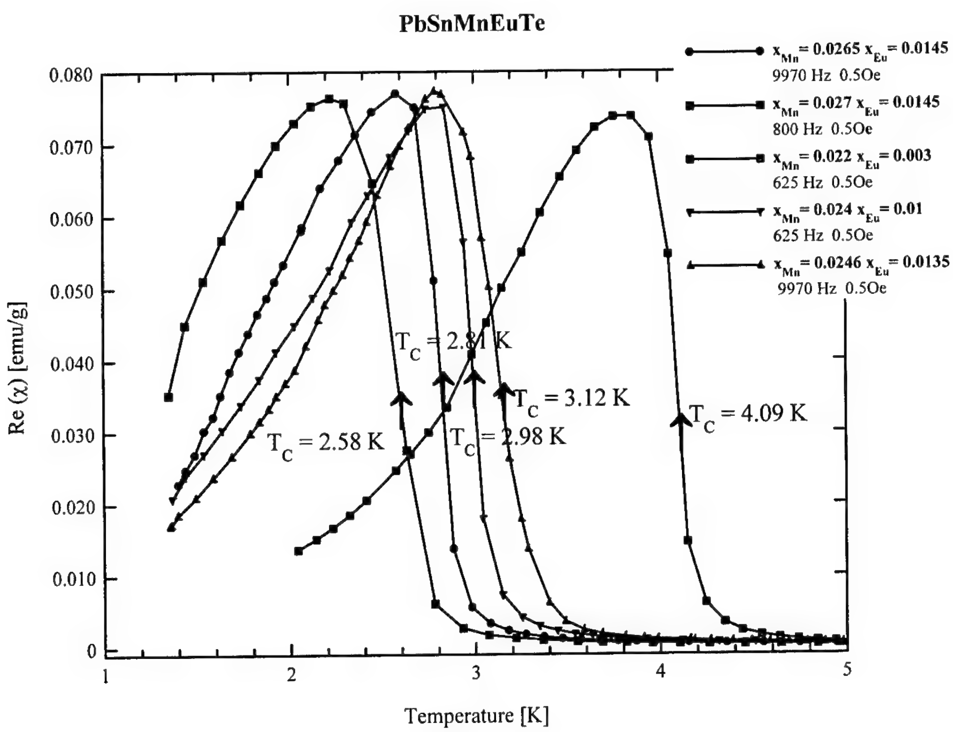

Fig. 9. Magnetic susceptibility vs temperature in a series of $Pb_{1-x-y-z}Mn_xEu_ySn_zTe$ samples. Arrows indicate the temperatures of paramagnet - ferromagnet transition.

In magnetic metals and semiconductors, in addition to the normal part proportional to the magnetic field, the Hall resistivity contains a supplementary part proportional to the magnetization which is called anomalous Hall resistivity: $\rho_H = R_0 B + R_S M$, where R_0 and R_S are the normal and anomalous Hall coefficients, respectively, B is the magnetic field and M the magnetization. While the normal Hall effect results from the Lorenz force, the anomalous Hall effect (AHE) is due to the spin-orbit coupling in presence of spin polarization. Recently the interest to the AHE is growing due to the importance of the spin polarization and spin-orbit interaction in spin electronics.

We have undertaken measurements of anomalous Hall effect in $Sn_{1-x-y}Mn_xEu_yTe$ (x = 0.06 – 0.13 and y = 0.01 – 0.02) mixed crystals. In these crystals at low temperatures the phase transition to ferromagnetic /or spin glass-like phase takes place, driven by RKKY indirect exchange interaction mediated by free holes. The apparent hole concentration in our samples was of an order of 10^{21} cm^{-3} at room temperature. The magnetic properties of the $Sn_{1-x-y}Mn_xEu_yTe$ are determined by magnetic ions: Mn^{2+} (L=0, S=5/2) and Eu^{2+} (L=0, S=7/2). The measurements of the Hall effect were performed in magnetic fields up to 2 T in a continuous flow helium cryostat in the temperature range 2 K – 300 K. The Hall effect and electrical conductivity measurements were performed using a standard dc technique in the temperature range 4 K $\leq T \leq$ 300 K in magnetic fields B up to 1.6 T. Magnetic properties were studied using a Lake Shore 7229 Magnetometer/Susceptometer. Magnetization of the samples was measured at magnetic fields up to 9 T at the same temperatures as B dependence of the Hall effect.

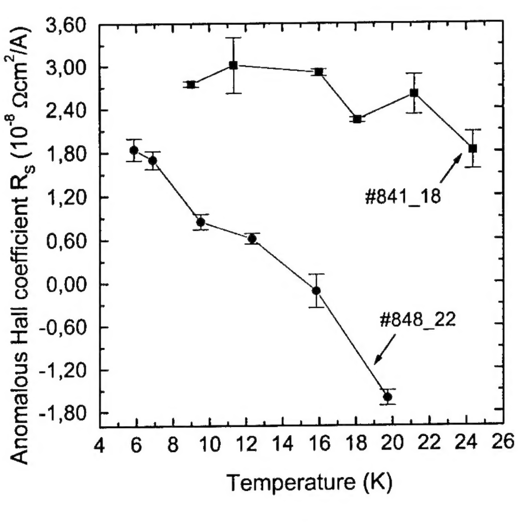

Fig. 10. Anomalous Hall effect coefficient for $Sn_{1-x-y}Mn_xEu_yTe$ samples #841_18 (Mn 13%, Eu 1%) and #841_22 (Mn 6%, Eu 2%)

Simultaneous analysis of the magnetization and transport data enabled us to determine the normal and anomalous Hall effect coefficients values. While the coefficient R_0 occurred to be practically temperature independent, the AHE coefficient R_S clearly depends on temperature (see Fig. 10). Such behavior was not observed previously in similar materials.[8] The results have been presented on the XXX International School on Physics of Semiconductors, *Jaszowiec 2001*, June 1 – 8, 2001, Ustroń-Jaszowiec, Poland. [5]

VIII. VISIT TO THE ARMY RESEARCH LABORATORY

A. Summary of the visit.

In September 2001 Dr. Małgorzata Górska visited the Army Research Laboratory, Adelphi, Maryland. She presented a seminar entitled "Interplay between Electronic and Magnetic Properties in IV-VI Diluted Magnetic Semiconductors". The talk was on recent results of our research and covered all the main topics described in the present report, in Sections II-VII.

The main conclusion of the talk was that there is a strong influence of the electronic structure on the magnetic properties of IV-VI Diluted Magnetic Semiconductors. As a result we observe new effects such as a carrier concentration dependent long range antiferromagnetic and ferromagnetic exchange interaction and a large contribution to the specific heat. These materials may in future give possibilities of application in magnetic sensors, thermoelectric power generators, and/or refrigerators. Further work on improving the electronic properties of the IV-VI DMS is needed. Preliminary results on heterostructures look promising.

Dr. Górska met with scientists form the ARL: Dr. Nibir Dhar, Chief of the IR Materials and Device Branch, and Dr. William Beck from this Branch. The results of the research presented here have been discussed as well as other topics such as infrared detectors and quantum dots. Dr. Górska visited some laboratories at the ARL: MBE facilities, material characterization laboratory, transport measurements facilities.

The second visit to the ARL took place on September 25, 2001. Dr. Górska met with Dr. Paul Amirtharaj, Chief of the Microphotonic Division and discussed M-S-M structures, M-S junctions, and nanostructures. She also met with Dr. Doran Smith, who is working on spintronics using magnetic resonance force microscopy. Dr. Kris Deb from the IR Materials and Device Branch was interested in possibilities of measurements of Raman scattering in IV-VI DMS. Dr. Deb received form Dr. Górska several samples of PbTe and $Pb_{1-x}Mn_xTe$ with x up to 0.04 and later has made preliminary measurements of Raman scattering.

B. Potential Collaborations with Scientists at the Army Research Laboratory

Several areas of mutual interest and possible collaboration were explored. These include:

(1) Raman spectroscopy on IV-VI diluted magnetic semiconductors with Dr. Kris Deb, who has already made preliminary measurements on some or our samples of PbTe and $Pb_{1-x}Mn_xTe$;

(2) Investigations of mobility-spectrum-analysis (MSA) techniques with Dr. William Beck. Work in this area is in progress at the Army Research Laboratory, the University of Maryland, and the Institute of Physics.
(3) Studies of spintronics with Dr. Doran Smith, who is investigating spin diffusion in the GaAs:Mn system. Possible collaborators include Prof. Robert Anderson at the University of Maryland. Spintronics research on the same materials is also underway at the Institute of Physics.
(4) Investigation of thermoelectric power in diluted magnetic semiconductor heterostructures with Dr. Paul Amirtharaj.
We anticipate that research in these four areas will form a basis for collaboration between the Institute of Physics and the Army Research Laboratory.

VIII. CONCLUSIONS

1. In $Sn_{1-x}Mn_xTe$ the exchange interaction among Mn ions may be both antiferromagnetic and ferromagnetic, depending on the free carrier concentration, i.e. the relative position of the Fermi level and the Σ valence band. In $Sn_{1-x}Gd_xTe$ the exchange is always antiferromagnetic, but it does depend on the carrier concentration and the Gd-content, and reaches a maximum at a hole concentration of about 3.1×10^{20} cm^{-3} in samples with $x \geq 0.025$. This "resonant" behavior is due the proximity of the Gd *5d* level to the top of the Σ valence band and the Fermi level.
2. Magnetic specific heat vs temperature in $Pb_{1-x}Mn_xTe$ shows a maximum about 1 K in zero magnetic field. The peaks' height is approximately the same in zero and nonzero magnetic field up to 4 T. The theoretical calculations have shown that to obtain such result one must take into account the magnetic ion system, the free carrier system, and the interaction between them.
3. $Pb_{1-x}Mn_xTe$ is a very promising material in thermoelectric devices, because of the large increase in the Seebeck coefficient with increasing Mn-content. However, in the ternary mixed crystals the carrier mobility decreases and that effect limits the thermoelectric figure of merit. Further development of the thermoelectric materials based on IV-VI DMS may be possible after obtaining crystals with a room temperature mobilities above 500 cm^2/Vs.
4. Thin films of $Pb_{1-x}Mn_xTe$ and $Sn_{1-x}Mn_xTe$ of good quality can be obtained by MBE technique on BaF_2 substrates. They have thermoelectric and magnetic properties similar to those in bulk materials; in particular the carrier concentration induced paramagnet – ferromagnet transition has been observed in $Sn_{1-x}Mn_xTe$ thin films.
5. New quaternary and quinary DMS show the magnetic interaction vs carrier concentration pattern similar to that observed in ternary DMS, but the dependence on the magnetic ion concentration is different in case of the Mn and Eu ions. A temperature dependent anomalous Hall effect has been observed in $Sn_{1-x-y}Mn_xEu_yTe$. These materials may be interesting from the point of view of spin electronics.

IX. PUBLICATIONS RELATED TO THE PROJECT

[1] ***"Magnetization of*** $Sn_{1-x}Mn_xTe$***"***
M. Górska, J.R. Anderson, C. Wolters, A. Łusakowski, T. Story, and Z. Gołacki
Phys.Rev. B **64**, 115210 (2001).

[2] ***"Magnetic specific heat of*** $Pb_{1-x}Mn_xTe$***"***
A. Łusakowski, A. Jędrzejczak, M. Górska, V. Osinniy, M. Arciszewska, W. Dobrowolski, V. Domukhovski, B. Witkowska, T. Story, and R.R. Gałązka
Submitted to Phys. Rev. B.

[3] ***"Thermoelectric power in ferromagnetic*** $Pb_{0.16}Sn_{0.72}Mn_{0.12}Te$ ***semiconductor"***
M.V. Radchenko, G.V. Lashkarev, V. Osinniy, B. Witkowska, V. Domukhovski, T. Story
Submitted to J. Magn. Magn. Mat.

[4] ***"Carrier induced ferromagnetism in epitaxial*** $Sn_{1-x}Mn_xTe$ ***layers"***
A.J. Nadolny, J. Sadowski, B. Taliashvili, M. Arciszewska, W. Dobrowolski, V. Domukhovski, E. Łusakowska, A. Mycielski, V. Osinniy, T. Story, K. Świątek, R.R. Gałązka
Submitted to J. Magn. Magn. Mat.

[5] ***"Anomalous Hall Effect in*** $Sn_{1-x-y}Mn_xEu_yTe$ ***Mixed Crystals"***
K. Racka, I. Kuryliszyn, M. Arciszewska, W. Dobrowolski, E.I. Slynko, V.E. Slynko
XXX International School on the Physics of Semiconducting Compounds, *Jaszowiec 2001*, Ustroń-Jaszowiec, Poland, June 1 – 8 2001. Abstract only.

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